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Remarkable Stabilization of Self-Assembled Organogels by Polymerization

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In recent years a number of low molecular weight organic compounds have been found to be effective gelators for organic solvents.^{1,2} They have in common that in organic solution they self-assemble into elongated fiber-like structures through highly specific intermolecular interactions. These fibers in turn form a three-dimensional network encapsulating the solvent. The well-defined molecular arrangement within the fibers³ offers ample opportunity for the development of functional gels.⁴ Large open network structures with, for instance, recognition sites or electron conducting groups open new possibilities in areas such as catalysis, sensor technology, and materials science. However, organogels commonly suffer from instability, for instance, due to crystallization or lack of mechanical robustness. Furthermore, despite major achievements in supramolecular chemistry to achieve controlled self-assembly of organic molecules,⁵ until now most low molecular weight gelators have been found by serendipity rather than by design. Very recently, Hanabusa and co-workers⁶ and our group⁷ succeeded in the systematic design of novel gelators for organic solvents by exploiting the self-assembling properties of urea groups.⁸ Here we report a novel polymerizable organogelator for organic solvents, based on (1*R*,2*R*)-*trans*-1,2-bis(ureido)cyclohexane, and the formation of highly stable organogels. These systems differ from macro-molecular gels⁹ in that the monomeric compound already forms gels through aggregation by extensive hydrogen-bond formation.

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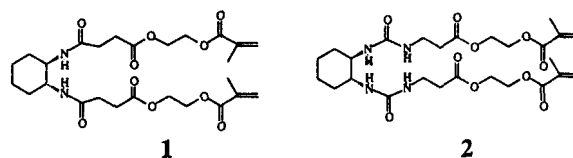
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Molecular modeling studies¹⁰ on *trans*-1,2-bis(acetamido)-cyclohexane and on *trans*-1,2-bis(3-methylureido)cyclohexane revealed that in these compounds both the amide and urea groups have severe steric interactions with the neighboring amide or urea group, respectively. In the most stable conformation of these compounds, both the amide or urea groups are rotated out of the plane of the cyclohexyl ring by about 60° and adopt an almost antiparallel coplanar orientation. As a consequence, the hydrogen-bonding moieties all are oriented along a common axis and, thus, strongly favor aggregation by hydrogen bonding in only one dimension. A translational aggregate of *trans*-1,2-bis(3-methylureido)cyclohexane, in which each molecule forms eight hydrogen bonds with its neighbors and is stabilized by 28.9 kcal/mol relative to the nonaggregated monomer, is shown in Figure 1. Most interestingly, these modeling studies revealed that both *trans*-1,2-bis(acetamido)cyclohexane and *trans*-1,2-bis(3-methylureido)cyclohexane can be functionalized at the methyl groups without interfering with the hydrogen-bonding arrangement. Thus, we prepared polymerizable bis(amido)cyclohexane and bis(ureido)cyclohexane derivatives **1** and **2** and investigated their gelating capacity for organic solvents. Compounds **1** and **2** are readily synthesized by addition of the corresponding, methacrylate-functionalized carboxylic acid or isocyanate to (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane.¹¹ Compound **1** was found to be soluble at room temperature in most of the solvents tested, but only in tetralin and at concentrations higher than 25 mg/mL gelation did occur. In contrast, compound **2** is insoluble in most organic solvents at room temperature, but at 50-80 °C the compound gradually dissolves. When these solutions of **2** were cooled to room temperature, optically transparent gels were formed with a variety of organic solvents including cyclohexane, butyl acetate, benzene, tetralin, and 1,2-dichloroethane. Gel formation occurred already at very low concentrations, typically 2-20 mg/mL, indicating that self-assembly of **2** is very efficient.¹¹ FTIR measurements revealed a shift of the NH stretch and amide I and II bands from 3390, 1655, and 1560 cm⁻¹ for a chloroform solution containing 10 mg/mL of **2** to 3310, 1632, and 1593 cm⁻¹, respectively, for a dried gel of **2**. These spectral changes indicate that upon gelation the urea groups of **2** become strongly hydrogen bonded.¹² Gels of **2** are only stable for 1-10 days, after which precipitation or crystallization occurs, and are easily disrupted by mechanical agitation. Gelation by **2** is, however, fully thermoreversible, and the melting temperatures of the gels are concentration and solvent dependent, as is commonly

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(10) Molecular modeling studies were performed using the CHARMM force field as implemented in QUANTA96 (Molecular Simulations Inc.). All calculations were done in the gas phase with a dielectric constant of 1 and a nonbonded cutoff of 15 Å with a switch function operating from 11 to 14 Å. Symmetry-averaged dipole preserving electrostatic potential derived point charges from AM1-optimized structures were used in all calculations.

(11) Compounds **1** and **2** are obtained as a white powder, and ¹H and ¹³C NMR (see the Supporting Information), FTIR, and mass spectral data as well as elemental analyses are in agreement with the structure. Full experimental details are given in refs 7b and 16.

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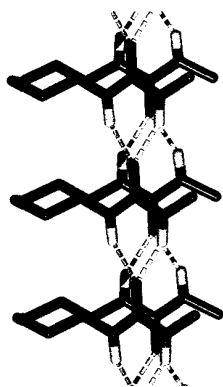


Figure 1. Model of translational aggregate of *trans*-1,2-bis(3-methylureido)cyclohexane (for clarity, nonpolar hydrogens have been omitted).

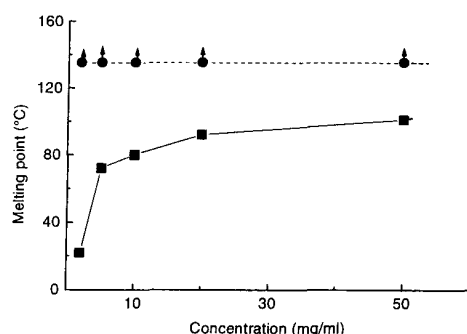


Figure 2. Melting temperatures of butyl acetate gels of **2** before (■) and after irradiation for 1 h (●), as determined by the dropping ball method.^{7b}

observed for organogels.¹³ A typical example for a butyl acetate gel of **2** is shown in Figure 2.

In a subsequent series of experiments, gels of **2** were prepared in the presence of 5 mol % of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone.¹⁴ Photopolymerization was achieved by irradiation with a 200 W high-pressure Hg lamp resulting in a slight increase of the turbidity of the gels, which reached a plateau after 2 h. FTIR of a dried gel showed the disappearance of the methacrylate CH vibrations at 3120 and 3050 cm^{-1} . Extraction of a dried gel with CDCl_3 did not give any monomer, as was evident from ^1H NMR analysis, indicating that irradiation for 2 h resulted in complete polymerization of gels of **2**. Polymerization resulted in a dramatic increase of the thermal stability of the gels, up to temperatures above the boiling points of the solvents (Figure 2). Even at concentrations of **2** as low as 2 mg/mL, the gel is stable up to at least 135 $^{\circ}\text{C}$, i.e., more than 100 $^{\circ}\text{C}$ above the melting point of the unpolymerized gel.^{15a} At these high temperatures, the gels did not melt or shrink; they also did not show any increase in turbidity. In all cases, they are perfectly stable. Photopolymerization of gels of **2** also resulted in an increase of the long-term stability. Whereas nonpolymerized gels of **2** in 1,2-dichloroethane start to crystallize after 1 h, the polymerized gel can be stored for months without showing any change in volume or turbidity. The increase in stability of gels of **2** upon polymerization is, most likely, enhanced by the fact that **2** contains two methacrylate moieties. Polymerization should therefore result in the formation of a highly cross-linked structure.

SAXS measurements of a concentrated gel of **2** showed a weak Bragg reflection at 28.3 \AA , indicating that **2** indeed

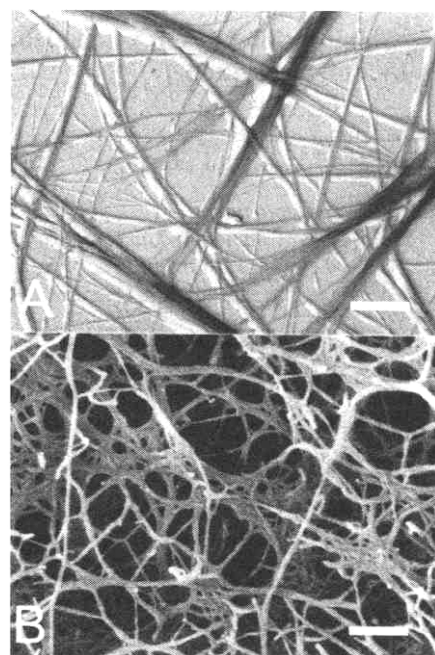


Figure 3. Transmission electron micrograph of a butyl acetate gel of **2** before polymerization (A, 5 mg/mL, Pt shadowed, bar = 1000 nm), and scanning electron micrograph of a benzene gel of **2** after irradiation for 1 h (B, 5 mg/mL, Pt coated, bar = 400 nm).

assembles into a well-ordered structure. A TEM photograph of a dried butyl acetate gel of **2** before irradiation is shown in Figure 3A. Many fairly straight thin fibers are observed, which occasionally fuse and intertwine. The diameter of the smallest fibers is approximately 50 nm, which is an order of magnitude larger than the spacing obtained from the SAXS measurements. Most likely, the fibers observed in the electron micrographs consist of bundles of hydrogen-bonded aggregates of **2**, similar to the structures observed in gels of other cyclohexyl bisurea gelators.^{6,15b} TEM studies of polymerized gels of **2**, however, failed because we were not able to deposit this material on formvar/carbon-coated grids in sufficiently thin slices. Therefore, polymerized gels were studied by SEM. An electron micrograph of a freeze-dried benzene gel of **2** after irradiation for 1 h is presented in Figure 3B. Polymerized **2** forms a highly cross-linked three-dimensional network of very thin fibers. The diameter of the thinnest fibers amounts to ~ 25 nm, which is significantly smaller than before polymerization. SAXS measurements revealed the presence of a weak first-order reflection at 20.7 \AA . Apparently, the gelator molecules in the fibers become more densely packed upon polymerization, which is most likely the result of the formation of covalent linkages between fibers.

The freeze-dried polymerized benzene gels of **2** give a highly porous material as is evident from the electron micrographs (Figure 3B). Separate experiments on larger samples revealed that almost no shrinkage occurred during the freeze-drying process and that the material retains its shape when removed from the vessel, in contrast to nonpolymerized samples which collapse to a denser structure. The white brittle material has an estimated density of only 0.005 kg/dm^3 and could be handled without deformation. The low density and the structure of the material give it all of the characteristics of an organic aerogel.¹⁶ The aerogels can be resoluted, even with other solvents such as methanol and chloroform, forming a optically transparent gel again, without changing its shape.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **1** and **2** (7 pages). See any current masthead page for ordering and Internet access instructions.

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